

# Reactivity of palm fatty acids for the non-catalytic esterification in a bubble column reactor at atmospheric pressure

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**Reactivity of palm fatty acids for the non-catalytic esterification in a bubble column reactor at atmospheric pressure**

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**Abstract**

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A bubble column reactor has been developed to produce fatty acids methyl esters by blowing superheated methanol continuously into triglycerides or fatty acids without using any catalysts at atmospheric pressure. In this paper, reactivity of variety fatty acids in non-catalytic methyl esterification using a bubble column reactor was investigated. Five kinds of fatty acids in palm oil (palm fatty acids), namely myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid were used as substrates. The reactivity of palm fatty acids was studied at 533 K in a semi-batch reactor system to produce variety of fatty acid methyl esters namely methyl myristate, methyl palmitate, methyl stearate, methyl oleate and methyl linoleate. The initial mass of fatty acid in the reactor was 200 g. The reaction started by blowing superheated methanol vapour continuously into the reactor at 4 g/min of methanol. After 60 min of reaction time, conversion of myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid at 523 K was 29, 38, 43, 48 and 47 (% mol/mol), respectively. While, the pseudo first order rate constant ( $k'$ ) of myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid was 0.0065, 0.0080, 0.0081, 0.0090 and 0.0095 min<sup>-1</sup>, respectively. In methyl esterification of palm fatty acids, reactivity of saturated fatty acids (myristic acid, palmitic acid, stearic acid) is lower than unsaturated fatty acids (oleic acid and linoleic acid), meanwhile in the saturated fatty acids, reactivity increased with the length of fatty acids alkyl chains.

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**Keywords:** Fatty acids, methyl esterification, biodiesel, non-catalytic, superheated methanol

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## Nomenclature

$C_{FA,0}$	fatty acids concentration at initial point of the reaction, [% mol/mol]
$C_{FA,t}$	fatty acids concentration at $t$ reaction time, [% mol/mol]
$C_M$	methanol concentration, [% mol/mol]
$dC_{FA}$	change in fatty acids concentration, [% mol/mol]
$dt$	change in reaction time, [min]
$k$	reaction rate constant defined by Eq. (3), [ $\text{min}(\text{mol}/\text{mol})^{-1}$ ]
$k'$	the pseudo first order rate constant defined by Eq. (4) and (5), [ $\text{min}^{-1}$ ]
$r_{FA}$	reaction rate of fatty acids, [ $(\text{mol}/\text{mol}) \text{min}^{-1}$ ]
$R^2$	coefficient of determination, [-]
$t$	reaction time, [min]
$T_{bn}$	normal boiling point, [K]
$\alpha$	conversion of the reaction, [% mol/mol]

## 1. Introduction

Biodiesel has been defined as the monoalkyl esters of long-chain fatty acids derived from renewable feedstocks, such as vegetable oils and animal fats, for use in compression-ignition (diesel) engines<sup>1</sup>. Biodiesel, consisting of fatty acids methyl esters (FAME) can be produced by transesterification of triglycerides (TG) and/or esterification of fatty acids (FA) with short-chain alcohol, mainly methanol. At present, most of the methods for transesterification reaction are using alkaline catalyst such as potassium hydroxide (KOH), sodium hydroxide (NaOH), sodium methylate (NaOCH<sub>3</sub>) and potassium methylate (KOCH<sub>3</sub>). The reaction occurs at moderate temperatures around 333 K and at atmospheric pressure with a short reaction time of around one hour<sup>2</sup>. However, this method has drawbacks such as difficulties in the recovery of glycerol (GL), the need for removal of the residual catalyst and the formation of saponified product (soaps) due to the excess of free fatty acids (FFA). This separation/purification adds operating and capital cost to biodiesel production.

The production of biodiesel from low-cost raw materials, which generally contain high amounts of FFA. The production of biodiesel from this kind of raw materials comprises a two-stage process, which requires an initial acid-catalyzed esterification of the FFA, followed by a base-catalyzed transesterification of the triglycerides. Commonly, the acid H<sub>2</sub>SO<sub>4</sub> is the catalyst on the first step of this process. It must be said, however, that major drawbacks such as substantial reactor corrosion and the great generation of wastes, including the salts formed due to neutralization of the mineral acid<sup>3</sup>.

To deal with the problems posed by impurities and post-process separation, many alternative processes have been suggested. These include pre-treatment with an esterification reaction with an acid catalyst to lower FFA<sup>4</sup>, reactions with enzymes<sup>5,6</sup>, direct reactions with a heterogeneous catalyst for easier separation<sup>7,8</sup> and non-catalytic reactions in supercritical methanol<sup>9,10</sup>. This last process is very interesting since the reactions occur without a catalyst and is less sensitive to water and free fatty acid than conventional homogeneous catalyst. The reaction was found to complete in a very short time (4 – 10 min). However, the reaction requires temperatures of 623 – 850 K and pressures of 43 – 105 MPa, which are not practical for application in industry.

Han et al.<sup>11</sup> used CO<sub>2</sub> as co-solvent to decrease the operating temperature, pressure and molar ratio of alcohol to vegetable oil. It was demonstrated that, with an optimal reaction temperature of 553 K, methanol to oil molar ratio of 24 and CO<sub>2</sub> to methanol molar ratio 0.1, a 98% yield of FAME was observed in 10 min at a reaction pressure of 14.3 MPa. Kusdiana, & Saka<sup>12</sup> had studied methyl esterification of FFA of rapeseed oil treated in supercritical methanol. Warabi et al.<sup>13</sup> have reported about alkyl esterification of FA in various supercritical alcohols (573, 6 – 20 MPa). The reaction temperature could be decreased but the reaction pressure was still high. The reactor costs will be expensive for their pressurized reactions and might lead to high energy consumption.

Yamazaki et al.<sup>14</sup> have developed a bubble column reactor (BCR) to produce FAME by blowing bubbles of superheated methanol vapour into oil (TG) without using any catalysts. Kinetics of the non-catalytic transesterification of palm oil at atmospheric pressure has been reported by Joelianingsih et al.<sup>15</sup> The effects of reaction temperatures (523, 543, and 563 K) on the rate constant, conversion, yield of FAME and composition of the reaction product under semi-batch mode operation were investigated. The performance of the BCR for the non-

catalytic methyl esterification of oleic acid has also been reported by Joelianingsih et al.<sup>16</sup> However, reactivity of variety FA via the non-catalytic methyl esterification in BCR has not been reported. The objective of this study is to investigate reactivity of five kinds of FA commonly found in palm oil (myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid) in semi-batch reactor system.

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**2. Materials and methods**

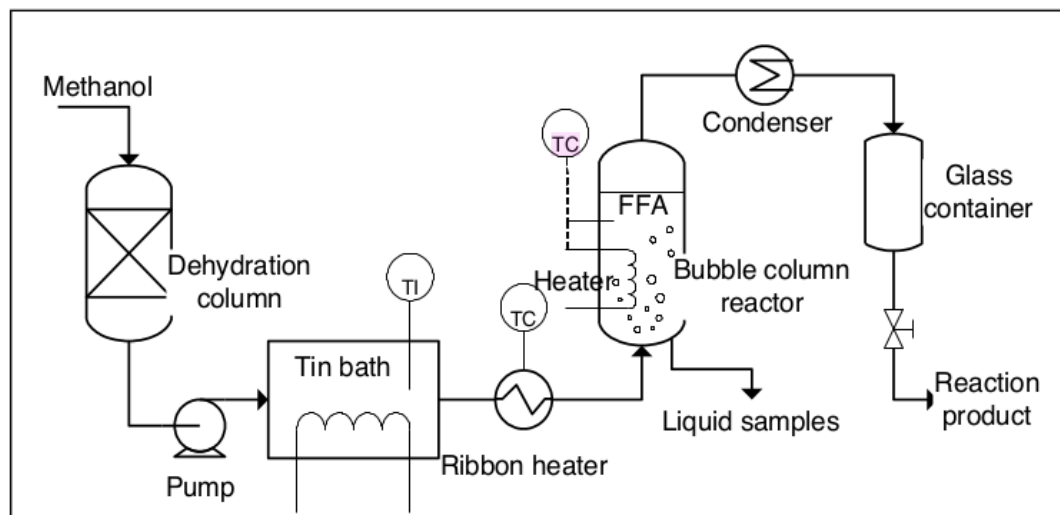
2.1 Materials

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 Oleic acid (OA), technical grade of minimum 90% w/w purity, as a substrate, was purchased from Sigma-Aldrich Inc. Myristic acid (MA) of minimum 98% w/w purity, palmitic acid (PA) of minimum 95% w/w purity, stearic acid (SA) of minimum 95% w/w purity, linoleic acid (LA) of minimum 88% w/w purity, and methanol HPLC grade, used as substrates, were purchased from Wako Pure Chemical Industries, Ltd.

Benzene and hexane (all HPLC grade), used in the thin layer chromatography/flame ionization detector (TLC/FID) analysis were purchased from Wako Pure Chemical Industries, Ltd. Benzene was used as the developing solution, and hexane as the solvent. Squalane (C<sub>30</sub>H<sub>62</sub>) as the internal standard was purchased from Sigma-Aldrich Japan K.K. Fatty acids (MA, PA, SA, OA, LA) and FAME (methyl myristate, methyl palmitate, methyl stearate, methyl oleate, and methyl linoleate), used as standards were purchased from Sigma Chemical Co.

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 2.2 Reactor for the non-catalytic methyl esterification

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 Fig.1 shows the schematic flow diagram of a reactor used in this experiment. This system has been used in our previous work for non-catalytic methyl transesterification<sup>15</sup>. The BCR was a four-necked flask (capacity, 500 mL) equipped with a condenser, a pipe for methanol vapour feed and a temperature controller (TC). The reactor was placed in a mantle heater. The glass dehydration column was filled with molecular sieves. A pump with a variable speed motor (model NPD – 461, Nihon Seimitsu Kagaku Co., Ltd.) was used to control the charging rate of methanol. A tin bath was placed on an electric heater. Temperature of the tin bath was monitored by a temperature indicator (TI). Temperatures of the superheated methanol supplied to the reactor and liquid in the reactor were controlled with the two TCs.



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 Fig. 1. The schematic flow diagram of the reactor used in esterification experiment.



The reactor was initially charged with 200 g of FA and heated to the desired temperature. Liquid methanol was pumped out of the dehydration column to the tin bath for vapourization. The methanol vapour was passed through a ribbon heater and the reaction started by blowing superheated methanol bubbles continuously into the reactor at 4 g/min of methanol. The temperature of superheated methanol feed was set up to the reaction temperature. The reacted products in the gas phase were condensed and collected in the glass container. The reaction products were taken from the glass container every 20 min and then weighed (samples A). During the reaction course (100 min), 5 samples were collected. Liquid samples in the reactor were taken 20 – 30 mg every 20 min to be analyze FAME and FA contents using TLC/FID. To study reactivity of palm fatty acids; MA, PA, SA, OA and LA were used as substrates and reaction was conducted at the same reaction temperature (523 K).

### 2.3 Methyl esterification procedure and conditions

The reactor was initially charged with 200 g of FA and heated to the desired temperature. Liquid methanol was pumped out of the dehydration column to the tin bath for vapourization. The methanol vapour was passed through a ribbon heater and the reaction started by blowing superheated methanol bubbles continuously into the reactor at 4 g/min of methanol. The temperature of superheated methanol feed was set up to the reaction temperature. Reacted products in the gas phase were condensed and collected in the glass container. The reaction products were taken from the glass container every 20 min and then weighed (samples A). During the reaction course (100 min), 5 samples were collected. Liquid samples in the reactor were taken 20 – 30 mg every 20 min to be analyze FAME and FA contents using TLC/FID. To study reactivity of palm fatty acids; MA, PA, SA, OA and LA were used as substrates and reaction was conducted at the same reaction temperature (523 K).

### 2.4 Analysis

Methanol and water contents in the gaseous products (sample A) were evaporated using a rotary evaporator and then the gaseous products without methanol and water were obtained (samples B). The samples B were weighed and their FA and FAME content were analyzed using TLC/FID.

TLC/FID was used to analyze the content of FA and FAME in the samples B and the liquid samples in the reactor. Analyses were performed with an Iatroscan MK-5 Analyzer (Iatron Laboratories, Inc.). The flame ionization detector used hydrogen and air with flow rates of 160 and 2000 mL/min, respectively. Type SIII Chromarods were used as thin layers. Before being spotted, rods were scanned as blank on the instrument to obtain the proper degree of hydration. The samples B and the liquid samples (20 – 30 mg) were diluted with 1 mL solvent (hexane containing 5 mg/mL of squalane) and 1  $\mu$ L of the solution was spotted on each rod. Five replicates were used for each solution. The rods were developed for 30 min (they were stored in a glass chamber in which the atmosphere was saturated with benzene vapour), oven dried at 333 – 338 K for 5 min and then analyzed by the Iatroscan. The mass fraction of methyl oleate and oleic acid in the samples B and the liquid samples taken from the reactor was calculated based on the concentration of an internal standard.

## 3. Results and discussion

The feedstock for biodiesel is usually a mix of different type of FA. Therefore, the knowledge of how different FA affects the reaction is important. This might also have an effect on the properties of fuel produced. Depending upon climate and soil conditions, different nations are looking into different vegetable oils for diesel fuels. For example, soya bean oil in the United States, rapeseed and sunflower oils in Europe, coconut oil in The Philippines, and palm oil in Southeast Asia (mainly Malaysia and Indonesia) considered as substitutes for diesel fuels<sup>17</sup>.

The fatty acids composition of refined palm oil is myristic acid (0.5–5.9), palmitic acid (32–47), stearic acid (2–8), oleic acid (34–44), and linoleic acid (7–12) %w/w<sup>15</sup>. Reactivity of five kinds of FA in palm oil for the non-catalytic esterification in semi-batch reactor system is described as follows.

### 3.1 The content of FAME in gaseous and liquid product

The content of FAME (% w/w) of methyl myristate (MM), methyl palmitate (MP), methyl stearate (MS), methyl oleate (MO) and methyl linoleate (ML) in the total mass (accumulated) of samples B (gaseous product) and

liquid in the reactor and the total mass of each fraction at 523K are shown in Tables 1 and 2, respectively. The principle of a BCR for transesterification of TG is the similar with a reactive distillation (RD), where the reaction products in the gas phase (GL and FAME) is continuously removed from the reactive zone while TG as the reactant still exist in the reactive zone (liquid phase)<sup>15</sup>. The application of reactive distillation for the esterification reaction in BCR at a temperature of 523 has a weakness that is nearly the same volatility between the FA and FAME. Therefore, FA and FAME distribute in the gas and liquid phase with a small difference in the composition. If the difference in boiling temperature of FA and FAME ( $\Delta T_{bn}$ ) is smaller, then the difference of FAME content in the gas and liquid phase will be smaller as presented in Tables 1 and 2. Table 3 shows the normal boiling point (the boiling point of component at atmospheric pressure ( $T_{bn}$ ) for pure FA and FAME of myristic, palmitic, stearic, oleic and linoleic<sup>18,19</sup>.

Table 1. The total mass of gaseous product and content of FAME in each reaction experiment.

t (min)	Myristic		Palmitic		Stearic		Oleic		Linoleic	
	Total mass of sample B (g)	FAME content (%/w/w)	Total mass of sample B (g)	FAME content (%/w/w)	Total mass of sample B (g)	FAME content (%/w/w)	Total mass of sample B (g)	FAME content (%/w/w)	Total mass of sample B (g)	FAME content (%/w/w)
	0	0	0	0	0	0	0	0	0	0
20	63.73	23	41.86	26	26.87	22	25.07	12	24.77	27
40	125.62	33	88.75	37	54.82	35	56.05	44	55.60	44
60	185.20	32	135.59	44	84.25	42	90.00	52	88.94	51
80			177.69	46	113.09	47	124.59	58	122.63	57
100					142.26	51	159.96	61	156.51	61

Table 2. The total mass of liquid in the reactor and content of FAME in each reaction experiment.

t (min)	Myristic		Palmitic		Stearic		Oleic		Linoleic	
	Mass of liquid (g)	FAME content (%/w/w)	Mass of liquid (g)	FAME content (%/w/w)	Mass of liquid (g)	FAME content (%/w/w)	Mass of liquid (g)	FAME content (%/w/w)	Mass of liquid (g)	FAME content (%/w/w)
	0	200.08	0	200.82	0	200.79	0	199.82	0	199.9
20	136.35	16	158.96	21	173.92	24	174.75	14	175.13	21
40	74.46	18	112.07	30	145.97	38	143.77	34	144.30	39
60	14.88	11	65.23	39	116.54	46	109.82	46	11.96	46
80			23.13	45	87.70	50	75.23	51	77.27	53
100					58.53	51	39.86	56	43.39	51

From the data in Table 2, it can be seen that the longer the carbon chain of fatty acids will have a residence time in the reactor longer. This is because the longer the carbon chain of fatty acids will have a normal boiling temperature higher so that it becomes more difficult to evaporate. As a result, the purity of FAME in the gas phase will also be higher as presented in Table 1.

Table 3. The normal boiling points and molecular weight of variety FA and FAME.

Component	Normal boiling point, $T_{bn}$ (K)		$\Delta T_{bn}$ (K)	Molecular weight (g/gmol)	
	FA <sup>(1)</sup>	FAME <sup>(2)</sup>		FA	FAME
Myristic	591.0	568.0	23.0	228.376	242.403
Palmitic	626.8	611.0	15.8	256.430	270.457
Stearic	643.0	625.0	18.0	284.484	298.511
Oleic	633.0	622.0	11.0	282.468	296.495
Linoleic	475.0 *	639.0		280.452	294.479

<sup>(1)</sup> Gunstone et al.<sup>18</sup> <sup>(2)</sup> Yuan et al.<sup>19</sup> \* Measured at 1.4 mmHg

### 3.2 Reactivity of palm fatty acids in the BCR

Reactivity of fatty acids is determined based on the conversion and the reaction rate constant. Fatty acids react with methanol to form FAME by the following esterification reaction as presented in Eq. (1).



where R is an alkyl group with chain length MA: C14:0, PA: C16:0, SA: C18:0, OA: C18:1

Conversion of the reaction ( $\alpha$ ) is defined by Eq. (2).

$$\alpha = (C_{FA,0} - C_{FA,t}) / C_{FA,0} \times 100\% \quad (2)$$

where  $C_{FA,0}$  and  $C_{FA,t}$  are concentrations of FA in the total system at the initial time of the reaction and after the reaction time of  $t$ , respectively.

The concentration expressed in % mol/mol of MA, PA, SA, OA and LA in the total system (samples B and liquid in the reactor) at 523 K are presented in Table 4 and conversion of MA, PA, SA, OA and LA at 523 K is shown in Fig. 2. Molecular weight data of variety FA and FAME are shown in Table 3.

Table 4. The concentration of FA in the total system (gas and liquid).

$t$ (min)	The concentration of FA (% mol/mol) in the total system				
	MA	PA	SA	OA	LA
0	100	100	100	100	100
20	83	79	77	86	79
40	74	68	64	64	61
60	71	62	57	52	53
80		55	53	46	46
100			50	42	43

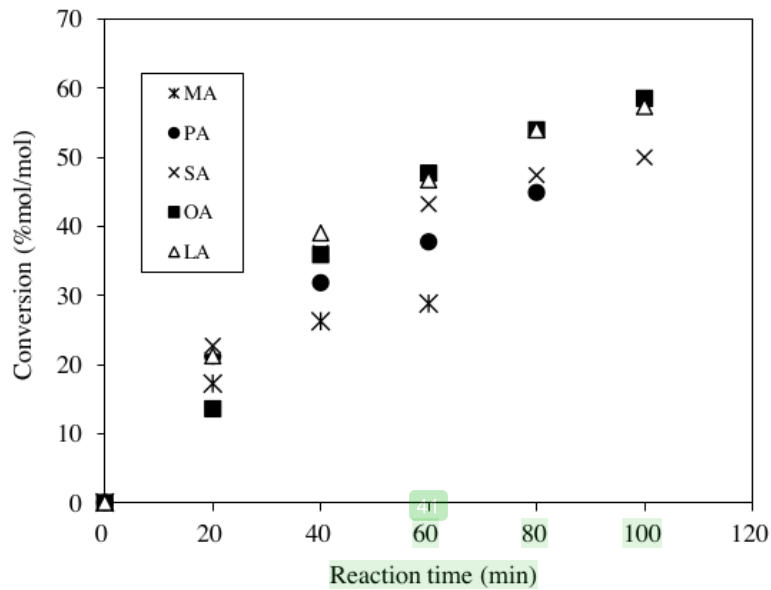


Fig.2. Conversion of the reaction of palm fatty acids at 523 K.

Another method to evaluate the reactivity of palm fatty acid is to calculate the rate constant of the reaction. In a semi-batch mode of operation where methanol (MeOH) is continuously passed through a reactor containing FA, the concentration of MeOH in the gas does not change appreciably. With the passage of reaction time ( $t$ ) the concentration of FA ( $C_{FA}$ ) will fall, but the concentration of MeOH ( $C_M$ ) will remain unchanged. If the kinetics is a first order with respect to both FA and MeOH, the reaction rate based on the decreased concentration of FA can be given by Eq. (3)<sup>20</sup>.

$$-r_{FA} = -dC_{FA} / dt = k C_{FA} C_M \tag{3}$$

Rearranging and integrating, noting that  $C_M$  is constant, the equation will be:

$$-\ln(C_{FA,t} / C_{FA,0}) = k' t \tag{4}$$

$$\text{where } k' = k C_M \text{ (the pseudo first order rate constant)} \tag{5}$$

Figures 3, 4, 5, 6, 7 show the relationship between the normalized concentration of FA ( $C_{FA,t} / C_{FA,0}$ ) and reaction times for MA, PA, SA, OA and LA, respectively at the same reaction temperature (523 K).



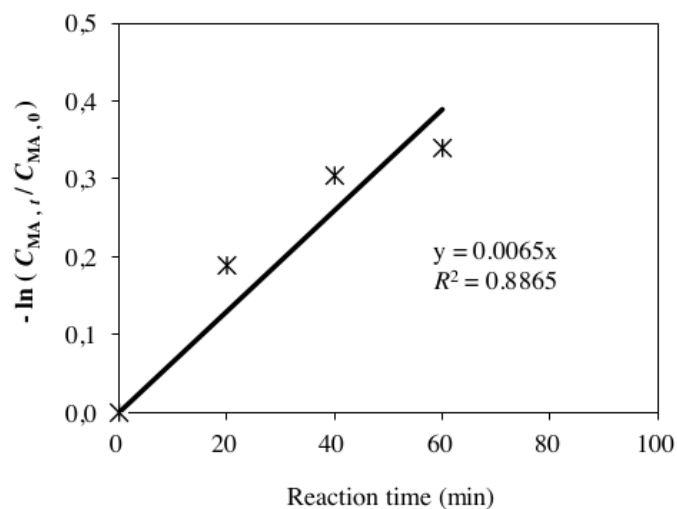


Fig.3. First order reaction model of MA esterification at 523 K.

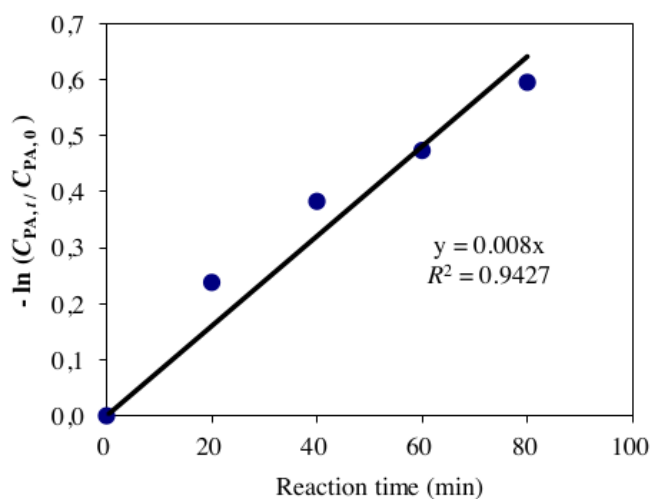


Fig. 4. First order reaction model of PA esterification at 523 K.

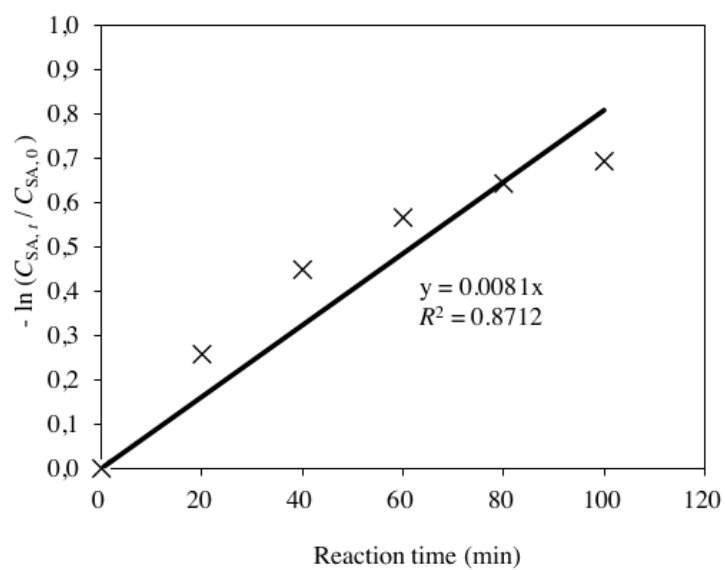


Fig.5. First order reaction model of SA esterification at 523 K.

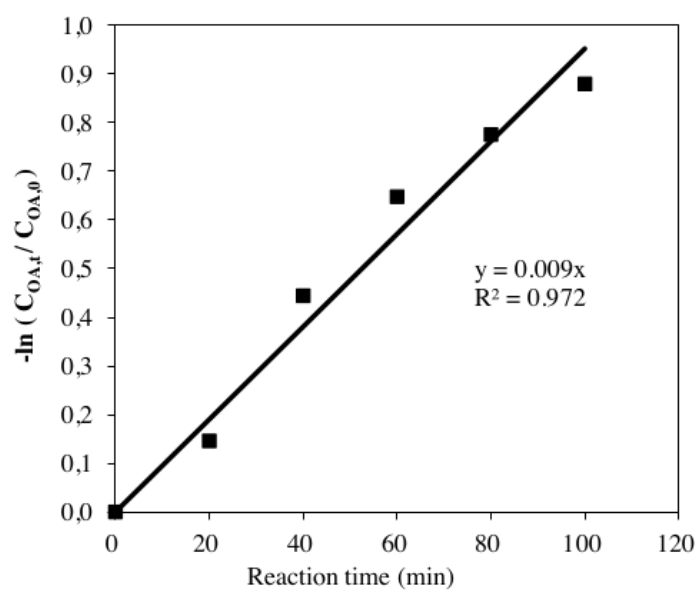


Fig.6. First order reaction model of OA esterification at 523 K.

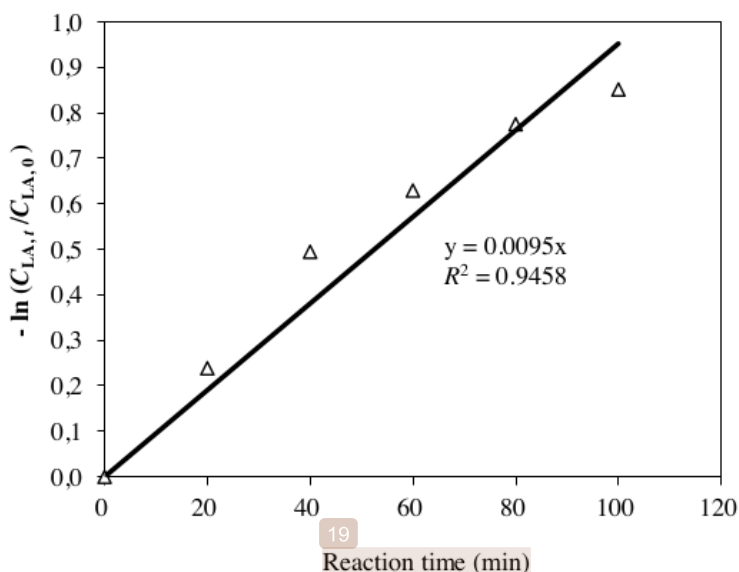


Fig.7. First order reaction model of LA esterification at 523 K.

The gradient of the linear regression of the  $-\ln(C_{FA,t}/C_{FA,0})$  curve with respect to the reaction time is regarded as the pseudo first order rate constant ( $k'$ ) according to Eq. (4). Table 5 gives the value of the pseudo first order rate constant ( $k'$ ) and coefficient of determination ( $R^2$ ) for each fatty acid.

Table 5. The rate constant of fatty acids methyl esterification.

Fatty Acids	$k'$ ( $\text{min}^{-1}$ )	$R^2$
MA	0.0065	0.8865
PA	0.0080	0.9427
SA	0.0081	0.8712
OA	0.0090	0.9720
LA	0.0095	0.9458

A substrate (fatty acid) is more reactive if the conversion of the reaction in semi-batch process is higher at the same reaction time and temperature, also the rate constant of the reaction is higher at the same reaction temperature. As shown in Fig. 2, conversion of the reaction of saturated fatty acids such as myristic, palmitic and stearic acids is lower than the unsaturated fatty acids such as oleic and linoleic acids. After 60 min of reaction time, conversion of myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid at 523 K were 29, 38, 43, 48 and 47 (% mol/mol), respectively. The reaction rate constant of the saturated fatty acids is lower than the unsaturated fatty acid as presented in Table 5. Thereby the saturated fatty acids show lower reactivity than the unsaturated fatty acid.

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These experiment results also consistent with results the reported by Aranda et al.<sup>21</sup> Their study of activation energy by semi-empirical methods revealed that the activation energy of palmitic acid (272 kJ/mol) is higher than that of oleic acid (176 kJ/mol), which means that the reactivity of palmitic acid is lower than the oleic acid. This might be assigned to the polarity of the double bond of oleic acid, which increases the reactivity of the carboxylic moiety. Warabi et al.<sup>12</sup> confirmed that saturated fatty acids (palmitic and stearic acid) have slightly lower reactivity than unsaturated ones (oleic, linoleic, linolenic) especially with ones containing more than one double bond. Based on the reaction rate constant value as shown in Table 5, linoleic acid has slightly higher reactivity than oleic acid.

Liu et al.<sup>22</sup> studied the effect of chain length in short chain carboxylic acids (acetic, propionic, butyric, hexanoic and caprylic acid) with methanol. The carboxylic acid reactivity decreased with increasing alkyl chain length. Their study is at temperature of 333 K and uses a commercial Nafion/silica composite solid acid catalyst (SAC-13) with initial concentration of carboxylic acid at 3M and 6M of methanol. They suspected that this trend was caused by two effects: an inductive effect and a steric effect<sup>23</sup>. The inductive effect is that electron-releasing ability increases with alkyl chain length, which helps the protonation of the carbonyl oxygen. At the same times the electrophilicity of the carbonyl carbon decreases, resulting in more difficulty for nucleophilic attack by alcohol. The steric effect is that smaller carboxylic acids are easier for alcohol to attack. These two effects support the lower conversion obtained with higher number of alkyl chain length of carboxylic acid<sup>22</sup>. Warabi et al.<sup>13</sup>, reported that their result also shows a slight difference between palmitic acid (C16:0) and stearic acid (C18:0), with the reaction being faster with shorter chain length.

Based on the conversion of the reaction as shown in Fig. 2 and the reaction rate constant in Table 5, for the saturated fatty acids; reactivity increase with the length of fatty acids alkyl chains. These results contradict with the results reported by previous investigators<sup>13, 22, 23</sup>.

As described in section 3.1, application of reactive distillation for the esterification reaction in BCR at a temperature of 523 K has a weakness that is nearly the same volatility between the FA and FAME. Conversion of the FA could not achieve 100% because FA evaporated as a product in the gas phase before reacting. There is a competition between reaction and evaporation of FA. In the saturated fatty acids, the normal boiling point increase with the length of fatty acids alkyl chains. The longer chain length of the FA makes the residence time in the reactor (reaction time) becomes longer, so that the conversion of the reaction and reaction rate constant was higher.

#### 4. Conclusions

Five kinds of fatty acid in palm oil could be methyl esterified in a BCR under atmospheric pressure at 523 K in the absence of a catalyst. After 60 min of reaction time, conversion of MA, PA, SA, OA, and LA was 29, 38, 43, 48 and 47 (% mol/mol), respectively. Meanwhile, the value of the reaction rate constant ( $k'$ ) of MA, PA, SA, OA, and LA was 0.0065, 0.0080, 0.0081, 0.0090 and 0.0095  $\text{min}^{-1}$ , respectively. In methyl esterification of variety of FA, reactivity of saturated FA is lower than unsaturated FA, meanwhile in the saturated FA, reactivity increased with the length of FA alkyl chains.

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